Movement of a secondary immiscible liquid in a suspension using a non-invasive technique

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Highlights

- Novel technique to monitor the movement of secondary immiscible liquid within a suspension of sucrose and sunflower oil.
- Achieved using a non-invasive method using X-ray CT, through a time lapse of scans.
- Movement of secondary liquid influenced by surface area to volume ratio.

Abstract

In this paper, the movement of a secondary immiscible liquid when added to a suspension of hydrophilic particles in a continuous hydrophobic phase is investigated. This was achieved through an approach using high speed camera and X-ray computer tomography. These non-invasive approaches allowed the secondary liquid displacement within the suspension to be monitored on the surface level and within the suspension through a time lapse of scans.

The addition of a small amount of secondary liquid to suspensions, can lead to a transition from a fluid-like to paste-like structure. The kinetics taking place and responsible for this, during both short and long term storage were investigated to better understand the mechanisms taking place. Water was added as the secondary immiscible liquid to suspensions composed of sucrose (icing sugar) and sunflower oil. Different volumes of secondary liquid were added to the suspensions. The rate of movement as well as the spreading of the secondary liquid into the suspension was calculated from the scans taken. The surface area to volume ratio was proposed as a reason for the spreading of the liquid for the smaller volume droplet being greater in comparison to the larger volume droplet.

Graphical abstract

Image for unlabelled figure

Keywords

X-ray μCT; X-ray computer tomography; Suspensions; Sucrose; Capillary action; Secondary immiscible liquid

Nomenclature

LIST OF SYMBOLS

d32Diameter of a sphere with same volume/surface area ratio [m]PcLaplace capillary suction pressure [Pa]rdContact radius of droplet with powder bed [m]RporsCharacteristic size of bed [m]V0Drop volume [m3]t'Volume of liquid penetrated at time t [s]ϕSphericity of the particles [dimensionless]εPorosity [dimensionless]μViscosity of liquid [Pa s]γLGInterfacial tension between liquid and gas [N/M]θContact angle [°]τCDAPenetration time for constant drawing area case [s]τDDAPenetration time for decreasing drawing area case [s]

1. Introduction

Many food products are composed of suspensions in which a solid phase (hydrophilic particles) is dispersed throughout a continuous liquid phase (hydrophobic liquid). An example of this is peanut butter spread. When small amount of a secondary immiscible liquid such as water is added to suspensions, the change from a fluid like material to a paste like material can be seen (Koos and Willenbacher, 2011). This change has been attributed to the formation of liquid bridges, between the secondary liquid and the primary particles which in turn alters the rheological properties of the suspension (Negreiros et al., 2015). The secondary liquid has a greater affinity to the primary particles in comparison to the continuous phase, due to their hydrophilic nature. The adhesive forces between the particles and secondary liquid are sufficient to allow the structure to maintain its shape, once a paste like material is formed. As well as the visual effects of adding small amounts of secondary liquids to suspensions, it has been shown that the rheological properties such as the yield stress and viscosity can increase several folds (Koos and Willenbacher, 2012). Also, this can lead to faster sedimentation, as with the addition of water, aggregates will form which settle due to gravitational effects (Yucel and Coupland, 2011).

Exposure of suspensions to high humidity environments, can also lead to major characteristic changes. This is of extreme importance to behaviour during manufacturing and processing of suspension based food produce in high humid environments, as this will ultimately affect the properties and shelf life of the end product. This is of particular importance, as from this phenomenon of moisture movement, microbial growth and chemical reactions within food products may occur, and thus lead to substantial food wastage (Ghosh et al., 2004). By understanding the kinetics occurring, this may allow for tailored food products which will help reduce wastage in the long term.

The addition of liquid to dry powder beds, for different compositions of hydrophilic and hydrophobic powder mixtures was studied by Nguyen, Shen (Nguyen et al., 2009) looking at the penetration time and shape of the droplets formed. It was shown that the material properties of the powder in terms of its hydrophilic/hydrophobic affinity greatly influence the penetration rate and granule formation.

For a suspension the movement of moisture can be from the environment or between the different domains within the suspension (such as the multi-domain food product, with a filling and outer coating e.g., wafer ice-cream), and will take place provided there is a concentration gradient

between the two in question. The recent work in the literature has been based on the assumption of diffusion being the dominant mechanism and basing models on apparent/effective diffusivities to simplify the mechanisms (Yuan et al., 2009 and Yuan et al., 2012). However, it is understood that it is more probable that a combination of transport mechanisms are taking place such as gravity, capillary and diffusion (Ghosh et al., 2004).

From the qualitative studies mentioned, it is difficult to follow the localised mass transfer of moisture. These studies only quantify and analyse the bulk mass transfers as an overall average of the sample and do not determine the kinetics of movement taking place locally. A non-invasive approach would allow for the mass transfer to be seen qualitatively thorough a sequence of images. These images can then be analysed in a quantitative manner.

Currently, there is no work which has been able to track and quantify the localised mass transfer of a secondary immiscible liquid within a suspension. The present work uses a novel non-invasive method of X-ray computer tomography to monitor the movement of a secondary liquid within a suspension, through a sequence of scans, taken at different time intervals. Through this new approach, it was possible to study the movement of a secondary liquid with time within a suspension. Thereby, allowing the kinetics to be quantified and better understood.

2. Materials and methods

2.1. Materials

Suspensions of sucrose (icing sugar, ZMR Zuckermühle Rupperswil AG, Germany) and high oleic sunflower oil (Surface tension 35.5 mN/m, FTA125. Viscosity 49 m Pa s, Malvern Kinexus lab+. Measured at 25 °C) were prepared by mixing using an overhead mixer (IKA, RW16) with a marine impeller (A100, Lightnin UK) at 650 rpm for 10 min. The mass fractions of the solid and continuous phase were 50 wt%. This was chosen so as to minimize the effect of settling of solid particles, while ensuring sufficient presence of the continuous phase to coat all the solid particles. The solid particles had a size distribution of 9–110 μm, with a d50 of 32 μm. This was measured by laser diffraction using Malvern Mastersizer S (Malvern Instruments, UK).

Suspensions once prepared were transferred into cellulose straws (9 mm diameter, Fishers Ideas UK) attached to a brass chuck designed for the X-ray μCT using a disposable pipette. A specially prepared lid with a hole in the centre to fit the pipette tip was then placed on top, to ensure the addition of the secondary liquid was to the centre of the sample. The secondary liquid, which was distilled water, was added to the surface of the suspension using an electronic pipette (Eppendorf Xplorer, UK), positioning the tip of the pipette close to the surface of the suspension but without actually touching the surface. The distance between the tip of the pipette and the surface of the suspension was approximately 5 mm. Once the secondary liquid was added, para-film was used to cover the hole to prevent the evaporation of the secondary liquid.

2.2. High speed camera

Tablets of sucrose were produced using the Instron testing machine (Instron 3367, USA). The compression force used was 6250 N, for a mass of 5 g in a 30 mm diameter die. Water penetration tests were conducted on these tablets with and without oil to see the initial capillary suction. High speed camera (Photron, 100KC) images were taken with a 1000 frame rate per second, to capture the droplet penetration into the tablet. A fixed volume of water (dyed with erythrosine B, for ease of identification) was deposited onto the surface of the tablet and the penetration of the droplet was recorded. The experimental set-up can be seen in Fig. 1.

Schematic of setup for penetration tests.

Fig. 1.

Schematic of setup for penetration tests.

2.3. X-ray μCT

X-ray μCT (micro-computer tomography) is a non-destructive technique which allows the internal microstructure of a sample to be seen. This is achieved through a series of projections which are taken as the sample is rotated between the X-ray source and detector. These projections are then reconstructed using algorithm which allows the 3D internal structure at the micron spatial resolution to be seen. The basic setup for this can be seen in Fig. 2.

Principle of X-ray μCT.

Fig. 2.

Principle of X-ray μCT.

All samples were scanned on the SkyScan 1174 system (Bruker microCT, Kontich, Belgium). Initial trail scans were conducted on a sample to find the optimum parameters in terms of voltage, current, exposure time and degree of rotations. The parameters chosen were changed to find a compromise between a relatively quick scans with sufficient resolution to capture the dynamics of the system taking place. Longer duration scans with higher resolution was possible, but due to the samples being scanned, this was not suitable for this particular case.

The spatial resolution of the scans was set to 11.4 μm. The system was operated at 50 keV, 800 μA with an exposure time of 1600 ms. Suspensions were positioned in cellulose straws (Fishers Ideas, UK) and rotated 180° in increments of 0.5°. One frame was taken at each step. The total scan time for each sample was 10 min 18 s. Several trial scans were conducted using various parameters (integration time, voltage, rotation step and spatial resolution) to find optimal conditions to capture

the dynamics of the system. A 10 min scan was suitable for this, to ensure the scan duration was fast enough to capture the dynamics taking place and of sufficient quality to distinguish water droplet from bulk suspension.

All scans were reconstructed using the algorithm provided with NRecon software (Bruker microCT, Kontich, Belgium). All reconstructed 3D datasets contained 1004 slices and a voxel size of 11.4 μm3.

X-ray scans were conducted on suspensions of sucrose and oil (50 wt% for both). Suspensions were transferred to the sample holder immediately after mixing. Scans were conducted every 30 min from 0 to 180 min (0 min refers to when the first X-ray scan was taken, 6 scans on each sample). Further scans were taken every hour from 180 min to 300 min. Scans were conducted every 30 min, to allow the completion of a scan and prepare the system to start the next scan. It was not possible to continuously scan one after another due to the operational procedure of the machine, when finishing one scan and starting another. Each scan took approximately 10 min. During this period of 10 min, the secondary liquid is moving and this needs to be taken into account when analysing the results. The secondary liquid was applied to the surface of the suspension using a pipette, after which para-film was used to cover the top of the sample to seal the environment. The time taken from adding the secondary liquid to beginning the X-ray scans was approximately 40 s.

Image slices from the scans were processed using the software Image J, to calculate the penetration distance of the secondary liquid (from the top of the suspension to the top of the secondary liquid) and the change in dimensions of the secondary liquid with time, which corresponds to the spreading of the secondary liquid. In Fig. 3 an example of the central slice along the x-axis for measuring the penetration distance and spreading of the secondary liquid can be seen. This slice chosen was when the secondary liquid is largest in terms of diameter. A schematic for the axis being mentioned can also be seen in Fig. 3.

(a) Schematic of axis in relation to sample and scans. (b) Measurement of ...

Fig. 3.

(a) Schematic of axis in relation to sample and scans. (b) Measurement of penetration distance. (c) Measurement of dimensions of secondary liquid.

3. Theory

3.1. Background

The penetration of a droplet into a dry porous bed is driven by the Laplace capillary suction pressure Pc (Eq. (1)) and is given by (Charles-Williams et al., 2011 and Hapgood et al., 2002):

equation(1)

equation(2)

where, γLG is the interfacial tension between the liquid and gas, θ is the contact angle, Rpore is the characteristic pore size of the bed, ϕ is the sphericity of the particles, d32 is the diameter of a sphere which has the same volume/surface area ratio in relation to the particles of interest, and ε is porosity.

The penetration of a liquid into a porous bed has two limiting cases which are commonly presented. These were described by Charles-Williams et al. (2011) as the constant drawing area (CDA) and decreasing drawing area (DDA), which can be seen in Fig. 4.

Penetration of liquid into porous bed (i) CDA, (ii) DDA (Charles-Williams et ...

Fig. 4.

Penetration of liquid into porous bed (i) CDA, (ii) DDA (Charles-Williams et al., 2011).

In the case of CDA, the contact angle decreases as penetration occurs, whereas in DDA the contact angle remains constant but the penetration is slower. For the case of CDA, as the area of contact is maintained, the penetration is the quickest. However, for DDA as the area of contact decreases progressively, the penetration time is slowest. In reality, the penetration is normally in between CDA and DDA.

The predicted time for liquid penetration (τ) based on the CDA and DDA is calculated using the Eqs. (3) and (4) (Hapgood et al., 2002):

equation(3)

equation(4)

τDDA=9τCDA,

where, V0 is the drop volume and μ is the viscosity of the liquid. It can be seen that the penetration of CDA is 9 times quicker than DDA.

The equations mentioned so far only deal with the movement of liquid into a dry powder bed, after complete penetration. When trying to understand the kinetics taking place, the movement of liquid with time is important, this will allow for modelled data to be correlated with experimental data to understand the mechanisms taking place. The volume of liquid penetrating into a powder bed can be calculated from Eq. (5), which assumes a CDA. For CDA, the radius of contact between the liquid and powder is assumed to be constant (Eqs. (5) and (6)) (Denesuk et al., 1993):

equation(5)

equation(6)

where, rd is the contact radius of the droplet with the powder bed and integrating from t'=0 to t' = t, which is the time taken for the specified volume of liquid to have penetrated into the powder bed.

3.2. Model-dry powder bed

The penetration of water into a suspension was modelled based on capillary movement. This was developed modelling the penetration of water into a powder bed of glass beads (model particles) with no oil phase (in air). The model of the penetration of 10 μl (1 × 10−8 m3) and 5 μl (5 × 10−9 m3) water droplet, into a dry powder bed of glass beads was conducted based on approaches used by Denesuk, Smith (Denesuk et al., 1993) and Hapgood, Litster (Hapgood et al., 2002) using an infinite number of pores. A diagram of how the pores and water penetration is modelled can be seen in Fig. 5.

Liquid droplet penetrating into a powder bed of infinite pores.

Fig. 5.

Liquid droplet penetrating into a powder bed of infinite pores.

For the input parameters, the surface tension (FTA 125), viscosity (Malvern Kinexus lab+) and porosity were obtained from experimental data. The d32 was obtained from the Mastersizer results, and a sphericity of 1 was used as the model is based on glass beads of spherical shape. The spreading radius was taken from the water droplet volume which has a radius of $1.335 \times 10{-}3$ m and $1.06 \times 10{-}3$ m for the 10 µl and 5 µl droplets, respectively. Rpore (characteristic pore size of bed) was calculated from Eq. (2), and k from Eq. (6). A dt−1 of 0.01 s was chosen initially as the penetration of the liquid based on capillary action is very fast. Porosity was calculated using the mass fraction of particles and continuous phase used. All input parameters used can be seen in Table 1.

Table 1.

Input parameters for calculating the volume of penetration rate into powder bed.

dt−1 (s−1)	0.01
Surface tension (N/m)—measured using FTA32	0.01
Advancing contact angle (°)	8.7
Viscosity (Pa s)	0.001
Porosity	0.565
d32 (m)	$3.3 \times 10{-}5$
Sphericity	1
Spreading radius (m)—radius of a 10 µl droplet	$1.335 \times 10{-}3$ (diameter = $2.67 \times 10{-}3$)
Spreading radius (m)—radius of a 5 µl droplet	$1.06 \times 10{-}3$ (diameter = $2.12 \times 10{-}3$)
Rpore (m)	$1.43 \times 10{-}5$
k	$1.47 \times 10{-}2$

The information from Table 1 was then used in Eq. (5) to plot the volume of liquid penetrated into powder bed against time which can be seen in Fig. 6.

Droplet penetration volume against time for water into a dry powder bed.

Fig. 6.

Droplet penetration volume against time for water into a dry powder bed.

It can be seen that it takes approximately 0.15 s and 0.10 s for the complete volume of 10 µl and 5 µl water droplets to penetrate into a dry powder bed, respectively. This was based on the constant drawing area case (CDA) which, as mentioned earlier, is the fastest in terms of penetration as the area of contact is maintained. For the slower case of decreasing drawing area (DDA), it would be approximately 9 times this time (≈1.35 s and 0.9 s).

The penetration distance with time is of more interest when looking at the kinetics. The graph of Fig. 6 can be improved to look at the penetration distance of the secondary liquid with time, by converting the volume into a diameter of the liquid penetrated based on a sphere for the secondary liquid. This can be seen in Fig. 7.

Droplet penetration distance against time for water into a dry powder bed.

Fig. 7.

Droplet penetration distance against time for water into a dry powder bed.

For a 10 µl and 5 µl droplet, the diameter is 2.67 mm and 2.12 mm, respectively. From Fig. 7, it can be seen it would take 0.15 s and 0.1 s for the complete droplet to penetrate and this will be compared to experimental data from this study.

This simple model was also based on a constant contact radius between the droplet and powder bed which is not completely accurate. However, it does highlight the time scales required for capillary effects for initial penetration when applied to the surface of a powder. The model was based on a droplet into powder bed surrounded by air, without any consideration for the continuous phase (sunflower oil) which will offer resistance to the penetration of the secondary liquid when applied to the surface. It is hypothesised that the capillary effect is only dominant when air is in contact with the liquid. Once the liquid droplet is completely immersed in the suspension and surrounded by oil, the capillary effect no longer exists as the capillary pressure is equal throughout the droplet and pushing in all directions equally and, therefore, the net effect is zero. The mechanisms responsible for the movement of a secondary liquid within a suspension are believed to be several and vary with time such as capillary, diffusion and gravity (Ghosh et al., 2004).

4. Results and discussion

4.1. High speed camera

The penetration of a 5 µl droplet onto a dry sucrose tablet can be seen in Fig. 8. The starting image, after the droplet came into contact with the surface of the tablet is shown along with the end image once the droplet is no longer visible on the surface and had fully penetrated. The experimental set-up used for this can be seen in Fig. 1. For the 5 µl and 10 µl water droplet onto a sucrose tablet, the time required for complete penetration of the droplet using this method was found to be 0.068 s and 0.113 s, respectively. The images for the 10 µl are not shown.

Water penetration of 5µl droplet on a sucrose tablet.

Fig. 8.

Water penetration of 5 µl droplet on a sucrose tablet.

An image was taken from above (along the z-axis, looking down) after complete penetration of the 5 µl water droplet using a microscope (Keyence, VHX-2000), which can be seen in Fig. 9. Image A from Fig. 9 is the original image, while image B is after applying a filter. In image B, the initial point of contact upon impact can be seen, which had an approximate diameter of 5 mm. After complete penetration the diameter of contact increased to 7 mm due to axial spreading. The experimental penetration time for both 5 µl and 10 µl was quicker compared to the modelled data in Fig. 6 which was based on a constant drawing area (CDA). The experiment indicates the drawing area increased rather than remaining constant and the spreading radius/diameter is double the value used in the model. This is believed to be due to the initial contact of the water droplet with the sucrose tablet, droplet which in this case is 5 µl (5 mm3), deforms into a hemisphere and therefore will have a larger radius/diameter in contact with the sucrose tablet in comparison to the radius/diameter of a sphere.

Image from above, showing region of contact for the 5µl water droplet on a ...

Fig. 9.

Image from above, showing region of contact for the 5 µl water droplet on a sucrose tablet. Scale on image is 500 µm.

A similar sucrose tablet was produced, which was covered in sunflower oil and left for a few hours to allow the oil to penetrate the pores of the tablet. After this, the penetration of a 5 µl water droplet was observed for which images can be seen in Fig. 10. The shape of the droplet on the tablet surface in Fig. 8 at time 0 s is similar to that seen in Fig. 10 at the start after initial contact. After 0.06 s which was the time required for complete penetration of the water droplet on the dry sucrose tablet, it can be seen for the tablet covered in sunflower oil, a large portion of the water droplet remains on the surface. Without the oil present, the water faces very little resistance from the air and therefore can penetrate very quickly. When the tablet and the pores of the tablet are covered in oil, the water has to displace the oil to proceed into the tablet, and this is believed to be the reason for the slower penetration time. It can be seen after 16 s in Fig. 10, the droplet has not completely penetrated the tablet and there is some axial spreading occurring. For the 10 µl water droplet similar spreading was seen after 16 s indicating the droplet has not fully penetrated the tablet. This shows with the introduction of oil into the system, the time for capillary suction of the droplet from the surface into the tablet is significantly increased.

Water penetration of 5µl droplet into sucrose tablet covered with sunflower oil.

Fig. 10.

Water penetration of 5 µl droplet into sucrose tablet covered with sunflower oil.

It should be noted for the experimental setup used; the water droplet will not only penetrate the tablet, but will also dissolve some sucrose as it penetrates the sucrose tablet. This will in turn increase the volume of the water droplet, and change the viscosity and density of the droplet. This was not considered for the simple model used in this case.

4.2. Secondary liquid—Water

The effect of changing the volume of secondary liquid (5 μl and 10 μl water) applied to the surface of suspension was investigated. As mentioned previously, the secondary liquid was deposited from a height of approximately 5 mm above the surface of the suspension. A time lapse of images for the 5 μl and 10 μl water can be seen in Fig. 11 and Fig. 12, respectively. It can be seen when comparing images from Fig. 11 and Fig. 12, the secondary liquid droplet is larger in Fig. 12 which is expected, as a greater volume of liquid was used.

Time lapse of central scans for suspension (5μl water). Scale on image at ...

Fig. 11.

Time lapse of central scans for suspension (5 μl water). Scale on image at 300-310 min is 1 mm.

Time lapse of central scans for suspension (10μl water). Scale on image at ...

Fig. 12.

Time lapse of central scans for suspension (10 μl water). Scale on image at 300–310 min is 1 mm.

The black region above the suspension is air, as has been shown in the image at 0–10 min in Fig. 11. The clear progression of the secondary liquid into the suspension can be seen in the time lapse of images in Fig. 11 for the 5 μl water. For the first two images shown (0–10 and 30–40 min) there is very little movement of the secondary liquid. After 60 min some clear movement of the secondary liquid can be seen, which increases as we progress through the time lapse of images. Also, as we progress through the images we can see the physical size of the droplet is increase indicating spreading of the water, and dissolving of sucrose within the water droplet. As the water droplet progresses into the suspension, a clear trail can be seen showing the path taken by the droplet. This can be seen clearly for the image at 300–310 min in Fig. 11. This path left behind is believed to be oil, as the sucrose which was present here has dissolved into the droplet and been taken with the droplet as it progresses. A similar trend can be seen for the images in Fig. 12 for 10 μl water as that mentioned for 5 μl water.

In Fig. 11, after 90 min, it can be seen a small oil layer has formed on the surface of the suspension. This slowly increases as you look through the sequence of images. This is believed to have formed due to the settling of the sucrose particles. After mixing the sample, it is then placed within the sample holder. As the sucrose particles are denser than the sunflower oil, they will naturally settle

with time. As mentioned previously, the mass fraction for both the sucrose and sunflower oil was chosen as 50%. The reason for this was to ensure that all the sucrose particles are covered in sunflower oil, without excess oil being present which will cause a layer to form on the surface after settling of the sucrose particles.

The images shown in Fig. 11 and Fig. 12 were used to calculate the penetration distance and the change in the dimensions of the droplet. The slice used was that for which the diameter of the secondary liquid is greatest. The penetration distance with time can be seen in Fig. 13 for the images in Fig. 11 and Fig. 12. It can be seen that the penetration distance with time is very similar for both volumes. The smaller volume secondary liquid (5 µl water) penetrated slightly quicker into the suspension between 90 min and 240 min, though for the scan taken at 300 min the distance was almost the same for both droplets.

Graph of distance penetrated by secondary liquid into suspension plotted against ...

Fig. 13.

Graph of distance penetrated by secondary liquid into suspension plotted against time (5 µl and 10 µl water). Error bars in the x-axis relate to duration (approximately 10 min) of each scan, during which droplet is still penetrating into suspension.

When looking at the images from Fig. 11 and Fig. 12 at 0–10 min, it can be seen that the water droplet is already completely immersed within the suspension and therefore the capillary action has already taken place. This is expected as from the modelled data, the time taken for this is less than 2 s and will therefore occur immediately after addition and be missed before the scans take place. Though the movement of the droplet into the suspension is continuing for the droplet, indicating other mechanisms are probably driving the droplet such as gravity and diffusion.

It should be noted that when looking at the penetration distance in Fig. 13, it is from the surface of the suspension to the top of the droplet as shown in Fig. 3. If considering the penetration distance from the top of the suspension to the bottom of the secondary liquid droplet an example for which can be seen in Fig. 14, the graph would look different as can be seen in Fig. 15.

Example of penetration distance measured from top of suspension to bottom of ...

Fig. 14.

Example of penetration distance measured from top of suspension to bottom of droplet.

Graph of distance penetrated by secondary liquid into suspension plotted against ...

Fig. 15.

Graph of distance penetrated by secondary liquid into suspension plotted against time (5 µl and 10 µl water). Penetration distance is from surface of suspension to bottom of secondary liquid droplet. Error bars in the x-axis relate to duration (approximately 10 min) of each scan, during which droplet is still penetrating into suspension.

When the modelled data from Fig. 7 is compared to the experimental data from Fig. 13 for the water penetration into a sucrose suspension, it can be seen that the penetration rate is substantially slower for the experimental data. For the modelled data, capillary action required less than 2 s, whereas for these scans conducted for this study required approximately 10 min each to complete and therefore it would not be possible to monitor this magnitude of movement in the period of time in question. Also, as the movement is proceeding at a much slower rate, this indicates other mechanisms are taking place such as gravity and diffusion.

It can be seen from Fig. 15 that the penetration distance is greatest for the 10 µl water droplet in comparison to the 5 µl water droplet. This is due to the 10 µl water droplet being larger and spreading more.

4.3. Secondary liquid—Velocity

The data from Fig. 13 was used to plot the velocity of the droplet from the surface of the suspension to the top of the secondary liquid droplet with time, which can be seen in Fig. 16. It can be seen for the 6 h period, in which the X-ray scans were conducted, the velocities of the droplets for both the 5 µl and 10 µl are fairly constant for between 1 and 6 h after addition, with the smaller volume droplet having a slightly higher velocity. The reason for this is believed to be due to the surface area to volume ratio of the smaller droplet (5 µl), which is larger in comparison to the bigger volume droplet (10 µl).

Graph of velocity of secondary liquid into suspension plotted against time (5µl ...

Fig. 16.

Graph of velocity of secondary liquid into suspension plotted against time (5 µl and 10 µl water).

For droplets of 5 µl and 10 µl water deposited onto a sample of sunflower oil only, the larger volume water will travel faster. However, for the case of a suspension of sucrose and sunflower oil, this is not the case. The reason for this is believed to be due to the presence on sucrose and the surface area of contact available between the sucrose and the water droplet. As the water droplet is progressing through the suspension, it can only continue to progress into the suspension by displacing or taking up the sucrose within its path. Thus, the smaller volume droplet, which in this case is the 5 µl droplet, had a higher settling velocity initially (between 90 and 240 min) in comparison to the larger 10 µl volume water droplet. Though after 240 min, the 5 µl and 10 µl droplets have a similar velocity. The reason for this is believed to be due to the smaller 5 µl droplet,

which is now full of sufficient sucrose to capacity, whereas the larger 10 µl droplet still has the ability to continue to take up sucrose and progress into the suspension. This agrees with the data shown in Fig. 17, where the increases in dimensions of the droplet with time were measured. The smaller volume droplet increased at a faster rate, in comparison to the larger droplet indicating a quicker uptake of sucrose from the bulk suspension. There is also potentially some compaction of the region below the droplet, as the droplet progresses into the suspension due to the density differences between the different phases, which may explain and contribute to the different settling velocities of the water droplets seen in Fig. 16.

Percentage increase in dimensions for the secondary liquid droplet within the ...

Fig. 17.

Percentage increase in dimensions for the secondary liquid droplet within the suspension against time (5 µl and 10 µl water). Error bars in the x-axis relate to duration (approximately 10 min) of each scan, during which droplet is still penetrating into suspension.

Fig. 16 would indicate that the droplet has reached a terminal settling velocity for the period being mentioned, though the droplet does slow down later on. The reason for this has been ascribed to the droplets ability to take up sucrose from the surrounding suspension. In the first 6 h period being monitored, the water droplet is able to continuously take up sucrose, as it has not been saturated yet. Though after a period of time, the droplet becomes saturated and will no longer be able to absorb any further sucrose and therefore not be able to proceed further into the suspension. This was confirmed by conducting scans on the samples after a longer period of storage. Scans were conducted on the 5 µl water droplet after 24 h and 52 h from addition, which can be seen in Fig. 18. The shape of the secondary liquid has changed significantly from the initial spherical shape, and the dimensions have changed from the initial scan at time 0 indicating significant spreading. The top surface of the secondary droplet has transformed into a flat surface, resembling a semi-circle shape. The flat top shows the secondary droplet as it progressed into its present location, was composed of liquid. This is evident from the flat top, as if it was a solid body, it would not deform into this shape.

Long term scans conducted on 5µl water droplet sample.

Fig. 18.

Long term scans conducted on 5 µl water droplet sample.

Also, the route taken by the secondary liquid to its position after 24 h can clearly be seen, when looking at the region above the secondary liquid. The sucrose particles have settled, creating a small oil layer surface which can be seen in Fig. 18. This is expected as the sucrose is denser in comparison to the oil, and therefore will naturally settle with time. Also, a clear path the secondary liquid droplet has taken can be seen to its present location within the figure. The path has remained, with the sucrose on both sides remaining and not collapsing in. Similar scans were conducted on the 10 µl sample after a longer period of storage, which showed similar behaviour. Images for these scans are not shown.

It should be noted that the suspension composition of 50 wt%. for both the sucrose and sunflower oil was chosen based on the size of the particles, to have sufficient oil to coat all of the particles with the continuous phase and minimise settling and thus a layer of oil on the surface. Should the mass fraction of sucrose be changed to a lower value, it may well be the case that the velocity of the larger droplet would be quicker as now the surface area to volume ratio of contact between the sucrose from the suspension and the water droplet is no longer significant in determining the settling velocity.

The distance from the surface of the suspension to the top of the droplet in Fig. 18 measures 4.52 mm, showing the droplet continued to progress even after the 6 h period shown for the images in Fig. 11. However, between the images shown in Fig. 18, there is a time difference of 28 h. In this 28 h period the droplet moved from 4.52 mm to 4.54 mm (0.02 mm), showing though the droplet is still continuing to move, it has slowed down considerably and the velocity has retarded dramatically compared to the earlier velocities shown in Fig. 16. This would indicate that the absorption kinetics between the sucrose particles and the water directly influence the velocity of the droplet. If a water droplet was deposited in a similar homogenous system with a fluid of similar viscosity and density, it would be expected that the water droplet would continue to progress once it had reached its terminal velocity, to the bottom of the sample, which was not the case for the system being studied here. Therefore, other forces are playing a part as well as the absorption of sucrose into the water droplet.

4.4. Secondary liquid—Droplet dimensions

The change in dimensions of the droplet with time from the images in Fig. 11 and Fig. 12, for the horizontal and vertical lengths can be seen in Fig. 19. For a 10 µl and 5 µl water droplet sphere, the projected diameter is 2.67 mm and 2.12 mm, respectively, which is similar to the points seen at time 0 in Fig. 19 for the horizontal and vertical lengths. It can be seen that the droplet is not perfectly spherical as the horizontal and vertical dimensions are different, and the difference between the two increases with time towards a more ellipsoidal shape.

Graph of the change in dimensions for the secondary liquid droplet within the ...

Fig. 19.

Graph of the change in dimensions for the secondary liquid droplet within the suspension against time (5 µl and 10 µl water). Error bars in the x-axis relate to duration (approximately 10 min) of each scan, during which droplet is still penetrating into suspension.

The horizontal length for both volumes showed the same trend of increasing indicating axial spreading. For the vertical length the same trend of increase is seen, though the vertical length is always smaller in comparison to the horizontal length as can be seen in Fig. 19.

In Fig. 17 the increase in % of the horizontal and vertical dimensions can be seen, with reference to the initial diameter for a perfect sphere of 10 μl and 5 μl which are 2.67 mm and 2.12 mm, respectively. It can be seen that when looking at the % increase in dimensions of the droplet, the greater increase was observed for the smaller volume droplet of 5 μl water. It is believed this is due to the greater surface area to volume ratio of the smaller secondary liquid droplet, which leads to a larger increase in change for the dimensions during the spreading of the droplet and dissolving of sucrose into the droplet in comparison to the larger droplet (10 μl water). The surface area to volume ratio is 3/radius for a perfect sphere, which corresponds 1.42 mm−1 and 1.12 mm−1 for the 5 μl droplet and 10 μl droplets, respectively.

After 300 min there is a 48% increase for the horizontal dimension and 39% increase for the vertical dimensions for the 5 μl droplet, whereas for the 10 μl droplet the increase is about 43% and 24% for the vertical and horizontal dimensions, respectively. This is a significantly larger increase for the smaller droplet in comparison to the larger droplet. The reason for this is believed to be due to the surface area to volume ration of the droplet. The smaller droplet has a larger ratio which enables it to increase in size easier, in comparison to the larger volume secondary liquid droplet.

When considering the horizontal dimension, the droplet is able to spread more in this direction due to the availability of sucrose in all directions. In the vertical direction, the sucrose is only available below the droplet. This is because above the droplet is either air or oil, and spreading in this direction would be going against gravity which is pulling the droplet down, due to water being more dense than oil. Also, as the droplet progresses vertically, it is hypothesised that it is compressing the region below of sucrose particles, which slows down its movement in this direction. This needs to be investigated through further experiments.

The change in volume of the droplet for the 5 μl and 10 μl droplet with time can be seen in Fig. 20. After 30 min, the 5 μl droplet has increased in volume more in comparison to the 10 μl droplet; however for points after 30 min the volume increase of the 10 μl droplet, is greater, which is expected, as the droplet is able to take more sucrose due to the larger initial volume.

Change in volume of secondary liquid droplet within the suspension against time ...

Fig. 20.

Change in volume of secondary liquid droplet within the suspension against time (5 μl and 10 μl water). Error bars in the x-axis relate to duration (approximately 10 min) of each scan, during which droplet is still penetrating into suspension.

Assuming that the increase in volume seen in Fig. 20, is due solely to the mass transport of sucrose from the suspension into the water droplet, and there is no diffusion of oil into the droplet or water away from the droplet, it is possible to calculate the change in sucrose concentration of the droplet with time. For a given volume of water to reach saturation with sucrose would result in a 126%

increase in volume at 20 °C (Bucke, 1995). From Fig. 20, it can be seen the time required for the 10 µl droplet to increase by 126% is approximately 240 min (initial volume of 10 mm3, increase of 12.6 mm3), whereas, for the 5 µl droplet the same is achieved in approximately 150 min (initial volume of 5 mm3, increase of 6.2 mm3).

The density of sucrose is 1588 kg/m3 and at 20 °C you can dissolve 2.0047 g of sucrose per gram of water to produce a saturated solution which equates to a 66 wt% concentration (Bucke, 1995). Using this information, the volume increase shown in Fig. 20 was converted to sucrose concentration of droplet, with time which can be seen in Fig. 21. It can be seen that the sucrose concentration of the droplet goes above the saturation solution at 20 °C, indicating that the droplet must contain both dissolved sucrose and solid sucrose. When preparing a saturated sucrose solution, it is known as you approach saturation it becomes more difficult to dissolve further sucrose and mechanical stirring is required. Whereas, for this case there is no mechanical stirring taking place and therefore, the dissolution rate of sucrose will be slower. Also, as the secondary liquid droplet progresses into the suspension, the viscosity and density will change as sucrose dissolves into the droplet, which needs to be considered for the dynamics taking place, though this is out of the scope of this paper.

Change in sucrose concentration of the secondary liquid droplet against time ...

Fig. 21.

Change in sucrose concentration of the secondary liquid droplet against time (5 µl and 10 µl water). Error bars in the x-axis relate to duration (approximately 10 min) of each scan, during which droplet is still penetrating into suspension.

The change in the surface area coverage of the secondary liquid droplet from the images in Figs. 11 and 12 against the depth penetrated can be seen in Fig. 22. As expected the surface area coverage for the 10 µl droplet is greater than the 5 µl droplet. What is of particular interest is the gradient of the experimental data, as this is an indication of the gradient of the channel left as the secondary liquid droplet moves into the suspension. The region of interest can be seen in Fig. 23 with the dashed line showing the particular gradient being referred to.

Change in surface area coverage of secondary liquid droplet with penetration ...

Fig. 22.

Change in surface area coverage of secondary liquid droplet with penetration into suspension.

Channel left behind after movement of secondary liquid into suspension.

Fig. 23.

Channel left behind after movement of secondary liquid into suspension.

4.5. Oil channel

From the tread line for both data points in Fig. 22, it can be seen that the gradient is greater for the 5 µl droplet. This indicates the dashed line is steeper for the smaller droplet, for which an example can be seen in Fig. 23. This channel still remains after 1 day as was confirmed through further scans and does not collapse in to fill the channel. The sucrose as mentioned already is denser than the sunflower oil and therefore naturally will settle. However, in this case the channel is strong enough to maintain its shape and hold the sucrose particles in place.

5. Conclusion

In this paper, movement of a secondary immiscible liquid droplet (water), when added to a suspension of hydrophilic particles (sucrose) in a hydrophobic continuous phase (sunflower oil) is investigated. The effects of different volume water droplets are investigated. It is shown through the combination of high speed camera and X-ray CT. It is possible to successfully track the movement of the secondary liquid, and through a sequence of X-ray CT scans, allow the kinetics of movement responsible for this migration to be better understood. Also, it is shown that the surface area to volume ratio plays a major role when considering the spreading of the secondary liquid.

Modelled data based on capillary action for a water droplet upon a dry powder of glass beads (in air), indicated a penetration time of less than 1.5 s for a 10 µl droplet and 0.9 s for a 5 µl droplet (based on DDA). Similar results were obtained for liquid penetration of water droplets onto a dry sucrose tablet. Longer times were recorded when the sucrose tablet was covered with sunflower oil, as now the water has to displace the oil to proceed into the tablet through capillary suction. After surface penetration, it is believed further mechanisms must be responsible which take place in conjunction with, or at a later stage after addition such as diffusion and gravity which need to be investigated further.

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